Surface consolidation of natural stones by use of bio-agents and chemical consolidate

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Abstract

Surface treatment is a frequently used method for conservation and restoration of building materials. . In this study, a novel and environment friendly strategy, bacterially induced calcium carbonate precipitation was applied to strengthen the surface of limestone. The treatment procedure for bio-deposition was first optimized regarding the aspects of treatment frequency and treatment time. Ultrasonic velocity was used to characterize the surface properties. It turned out that two subsequent applications of a one-step bio-deposition treatment had the best effect, where the transmitting velocity of the ultrasonic wave was increased with around 10~20%. The improvement mainly occurred from the surface till the depth of 4 cm and the largest increase was at the depth around 2 cm. Meanwhile, a commercial chemical ethyl silicate based consolidant, was applied under the same condition. Yet the efficiency measured by the increase in ultrasonic velocity was not significant.

Introduction

Buildings and monuments are susceptible to degradation processes, such as salt attack, biodeterioration, air pollution, etc., which result in a decline in mechanical, chemical and aesthetic properties. To preserve the architectural heritage, restoration and renovations are executed using techniques which are practical, economical, durable and ecological [1, 2]. Conservation is possible through cleansing, desalination or consolidation of the stone. Surface treatments, like application of a hydrophobic surface layer or graffiti protecting coatings are also options [3]. In this study, bacterially induced $CaCO_3$ precipitation was investigated to strengthen the surface of limestone. It is well known that most bacteria can induce the formation of $CaCO_3$ if given suitable conditions [4]. This biogenic-$CaCO_3$ is regarded as an environmentally friendly and economical material for engineering applications. Moreover, it has a better compatibility with the inorganic materials matrix than those organic chemicals which are currently used for surface protection and consolidation [5-7]. The $CaCO_3$ can plug the pores and/or form a continuous water-proof coating to hinder the penetration of corrosive substances, resulting in improved surface properties.

In this research, a carbonate precipitating bacterium, *Bacillus sphaericus*, was used to induce the formation of $CaCO_3$. This is an ureolytic strain, which can decompose urea ($CO(NH_2)_2$) into ammonium (NH_4^+) and carbonate (CO_3^{2-}). The latter then promotes the deposition of $CaCO_3$ in a Ca rich environment. The aim of this study is to use this in situ formed bio-$CaCO_3$ to fill the pores and/or form an extra dense layer on the surface/in the matrix of the limestone, and hence improve the surface properties.

Materials and Methods

Maastricht Limestone. The Maastricht limestone has a pale yellow color and consists mostly of microfossils and sand-size fragments of microcrystalline carbonate. It is a soft bioclastic calcarenite of the Upper Cretaceous age belonging to the Maastricht formation that has surfaced in southern Limburg being part of Belgium and the Netherlands. The Maastricht stone is mostly used for restoration purposes and is one of the few native Dutch natural stones that is still used in the building industry [8]. The material is very homogeneous, which makes it ideal for lab use. The sub-angular grains consist primarily out of sparitic calcite, which are skeletons of sea organisms and shell fragments. A remarkable property is the large frost resistance of the stone due to its coarse pore structure (dominant size of pores is 46 µm). The material also has a large durability [8]. The density is around 1400 kg/m³ and the average porosity is 47.5 %. The calcium carbonate content is around 98 % [9,10].

The limestone block was cut into small pieces with a size of 40 mm × 20 mm × 100 mm. Before the treatments, the specimens were pre-conditioned in an air-conditioned room (20±2 °C, 60%RH) until the weight changes were less than 0.1% within 24 hours intervals. The front surface (40 mm × 20 mm) was chosen for treatment. During the treatment, other side surfaces were covered with aluminum foil to prevent the contact with air and to simulate in situ conditions.

Tetraethyl orthosilicate (TEOS) consolidant. An ethyl silicate based solvent-free stone strengthener was used, that has been designed specifically for limestone. The product reacts with water that is present in the pores and forms amorphous, water-containing silica gel (aqueous SiO_2), which functions as binding agent (Eq. 1).

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$

TEOS has a SiO_2 gel deposit rate of approximately 30 % and its reaction speed is dependent on the humidity and temperature of the environment. The reaction takes about three weeks under standardized circumstances (20°C and 50 % RH), but reaches an optimum when the temperature is between 10 and 20 °C. The treatment cannot be applied if the temperature drops below 5 °C. The silica gel is weather resistant and has a high UV stability. There are no by-products that damage the building and large penetration depths can be achieved.

Bacterial strain and cultivation. *Bacillus sphaericus* LMG 22257 (Belgian Coordinated Collection of Microorganisms, Ghent) was used in this research. Selection of this bacteria was based on our earlier research [11,12], which shows that this strain has a high urease activity (40 mM urea hydrolyzed. $OD^{-1}\,h^{-1}$) and a high calcium carbonate production. The bacteria were grown in a sterile medium consisting of yeast extract (20 g/L) and urea (20 g/L) for 24 hours on a shaker (120 rpm, 28 °C). The grown culture was then used for the following bio-deposition treatment. The concentration of the bacteria in the culture was around 10^8 cells/mL.

Biodeposition and chemical treatment. All treatments were applied through capillary absorption. A volume of 150 mL solution (used for treatment) was first poured into a petri dish (d = 150 mm) and the solution level was around 9 mm. Two plastic bars (d = 2 mm) were placed in the petri dish as a support for the stones. The surface to be treated (face down) can therefore contact with the solution without touching the bottom of the petri dish. About 7mm of the specimens was directly immersed in the solution. Therefore, the penetration of the treatment agents into the specimens was mainly by means of capillary force.

For biodeposition, a two-step treatment was first investigated according to previous research [13,14]. The specimens were first placed in the bacterial grown culture for 4 or 20 s and then in a precipitation medium for 6 or 40 s, respectively. The precipitation medium, which was optimized based on $CaCO_3$ precipitation performance of bacteria, consisted of urea (1.11 M) and Ca-formate (1.11 M). In the meantime, a one-step treatment was explored. The bacterial cells from the grown culture were first centrifuged (7000 rpm, 7 min) and resuspended in the precipitation medium.

Subsequently, the stones were placed in the obtained mixture for 10 s or 1 min. The treatment was carried out on the same specimen twice or three times.

The chemical treatment was similar to the one-step biodeposition treatment. The specimens were placed in the ethyl silicate for 10 s or 1 min. The treatment was only applied once. As control, the stones were also treated only by pure water or the precipitation medium. The aluminum foil was removed one week after the treatment. All treatments were performed in triplicates.

Ultrasonic measurements. The ultrasonic measurements were performed seven days after treatment. An ultrasonic pulse velocity tester, with exponential 55 kHz transmitting/receiving probes, was used. The measurements were performed each 5 mm over the depth of the stone. The probes were placed 20 mm form the bottom of the stones (Fig.1). The device was regularly calibrated with a 51.6 µs calibration rod. The ultrasonic measurement device sends a 55 kHz pulse from the transmitter to the receiver. The time needed for the pulse to travel from the transmitting end to the receiving end is given by the device. By measuring the dimensions of the stone, the travel time could then be converted to a travel velocity. The transmitting velocity before and after the treatment can therefore be calculated. The wave travels fastest in solid, followed by liquid and gas. With formed precipitates on the surface and in the matrix, the velocity was expected to increase. Therefore, the efficiency of the treatment was indicated by the increase in velocity which was defined as follows.

$$R = \frac{V_a - V_b}{V_b} \times 100\% \tag{2}$$

Where:

R = relative change in transmitting velocity (%)

V_a = transmitting velocity after treatment (km/s)

V_b = transmitting velocity before treatment (km/s)

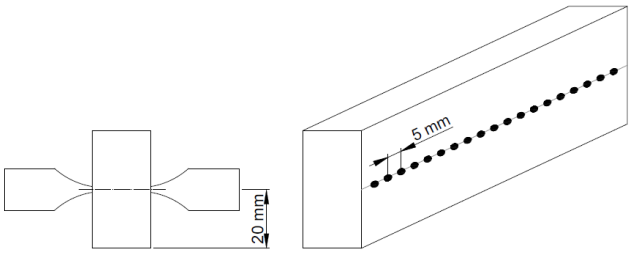

Fig.1. Position of the ultrasonic measurements on the stone; the front surface has been treated

Results and Discussion

The velocity of the ultrasonic wave transmitting the specimens before and after different treatments is shown in Fig.2 to Fig.8. The depth in the graphs was counted from the treated surface (d = 0). Three replicates a, b, and c were used for each kind of treatment. The treatment time was either 10 s (A in the figures) or 1 min (B in the figures). The relative change in transmitting velocity after treatment is also summarized (C in the figures).

The moisture content of the matrix influences the transmission velocity of ultrasonic waves. The velocity of a sound wave through water is 1.48 km/s [15], which is lower than that through solid limestone and higher than that through air. Therefore, the higher the moisture/water content in the matrix, the higher the velocity due to the water filled pores. However, after a short contact with water, either 10 s or 1 min, the change of the velocity was quite limited. As shown in Fig.2C, the difference in velocity before and after water contact was not significant. Nonetheless, to minimize the effect of initial moisture content on comparison, all specimens were pre-conditioned in a room with a stable temperature (20°C) and relative humidity (60%) at least 3 weeks before and after the treatment. Since moisture in the specimens is needed to react with ethyl silicate to generate the consolidant (Eq.1), complete drying of the specimens prior to treatment was not applicable.

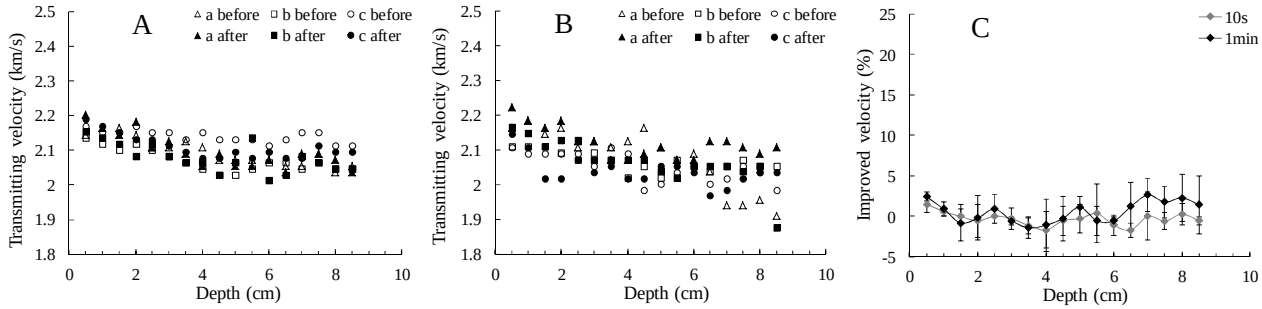

Fig.2 Ultrasound velocity in specimens immersed in water for 10 s (A) and 1 min (B), and velocity change (C)

The treatment by the precipitation medium without bacteria resulted in a slight increase (0~5%) in velocity for 10 s treatment and a slight decrease (0~3%) for 1 min treatment (Fig.3). While all bio-deposition treatments resulted in more obvious increase in transmitting velocity. The pronounced increase (10~15%) mainly occurred from the surface till the depth of 4 cm. Deeper than 4 cm, the increase was not so significant anymore (only around 5%). The largest increase in velocity was noticed at around 2 cm depth. The two-step bio-treatment showed very limited superiority over the one-step treatment. The overall velocity increase was 5~15% for the two-step bio-treatment and was 1~12% for the single one-step treatment (Fig.4 and Fig.5). When the one-step bio-treatment was applied two times, the velocity increase from depth 0 to 4 cm was enlarged to 10~20 % (Fig.6). However, further increase was not observed after the triple one-step bio-treatment (Fig.7), which had a similar velocity increase as the double one-step treatment. Moreover, prolonging the contact time with the treatment solution from 10 s to 1 min did not further improve the treatment efficiency.

The small variation in the transmitting velocity of the specimens in the precipitation medium without bacteria could be due to the remains of Ca salt in the pores and/or the moisture changes in the matrix after contacting with the medium. The variation along the whole depth was rather homogenous compared to the samples subjected to the bio-deposition treatments, in which the increase of velocity was assumed to be due to the precipitation of bacterially induced calcium carbonate inside the matrix. And hence, the treatment efficiency was dependent on the amount of biogenic-$CaCO_3$. The improved relative velocity changes at the different locations can also indicate the distribution of the precipitated $CaCO_3$ along the whole depth of the specimen, which was determined by the penetration of the bio-agents. During the two-step treatment, bacterial cells were absorbed into the pores of the stone in the first step, followed by the absorption of the precipitation precursors (urea and Ca source). Precipitation started after the bacteria met with urea and Ca^{2+}. While in the one-step treatment, the bacterial cells were pre-mixed into the precipitation medium and therefore the cells and precipitation precursors reached the matrix at the same time. Overall, the penetration time for bacteria was the same in these two treatments while for precipitation precursors the time was shorter in the two-step treatment. Theoretically, therefore the one-step treatment could be more efficient than the two-step treatment. However, no significant difference was observed. The reason could be that the difference in the amount of $CaCO_3$ formed in the two conditions due to a different penetration time and contact time was not large enough to create a significant difference in ultrasound transmission time. An improvement was seen after the repetition of the treatment, which was indeed due to penetration of more cells and precipitation precursors into the stone, and hence more precipitation could be formed. Yet, no further increase in velocity was noticed after the triple treatment. Since the specimens were far from saturation, further absorption of cells and precipitation precursors from the medium was expected, resulting in more $CaCO_3$ formed. Nevertheless, no further improvement was observed. This could be attributed to the sufficient consolidation of the stone after the double treatment, creating shortest route through the solid material for the waves.

In all bio-deposition treatments, the significant increase in velocity mainly occurred at depths below 4 cm and the largest increase was at the depth around 2 cm. The reason could be that bacteria started to induce the deposition of $CaCO_3$ during the penetration process. The newly formed particles

in the pores created extra barriers for the further penetration of the bio-reagents. Therefore, the penetration rate gradually decreased along the depth. The farthest location the bio-reagents could reach was around 4 cm deep. It should be noted that the precipitation did not occur immediately at the beginning of penetration. As time went on, deposition started and $CaCO_3$ accumulated. The plugging effect from the accumulated particles greatly hindered the further penetration of the bio-reagents. A further quantification of the actual amount of $CaCO_3$ precipitation at each location is needed in future research.

No improvement in the specimens treated with ethyl silicate was observed in this study (Fig.8). The reasons could be that there was not enough moisture inside the matrix to react with ethyl silicate and/or not enough ethyl silicate penetrated inside due to a short treatment time.

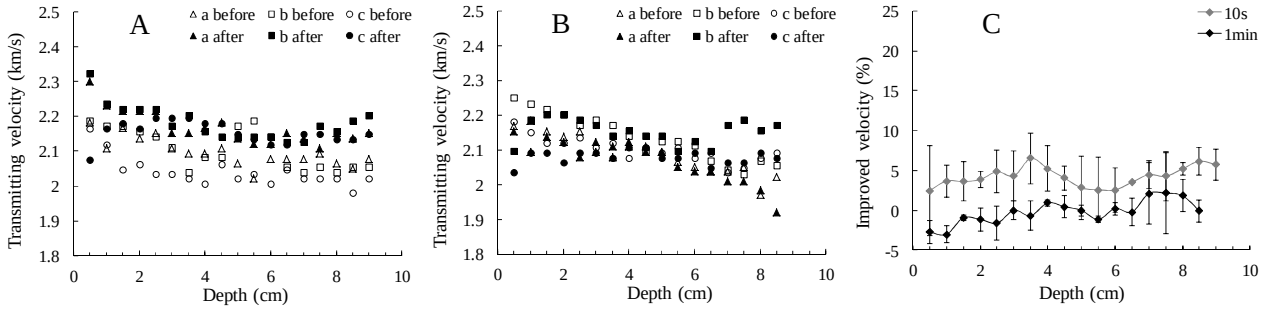

Fig.3 Ultrasound velocity in specimens immersed in the precipitation medium without bacteria for 10 s (A) and 1 min (B), and velocity change (C)

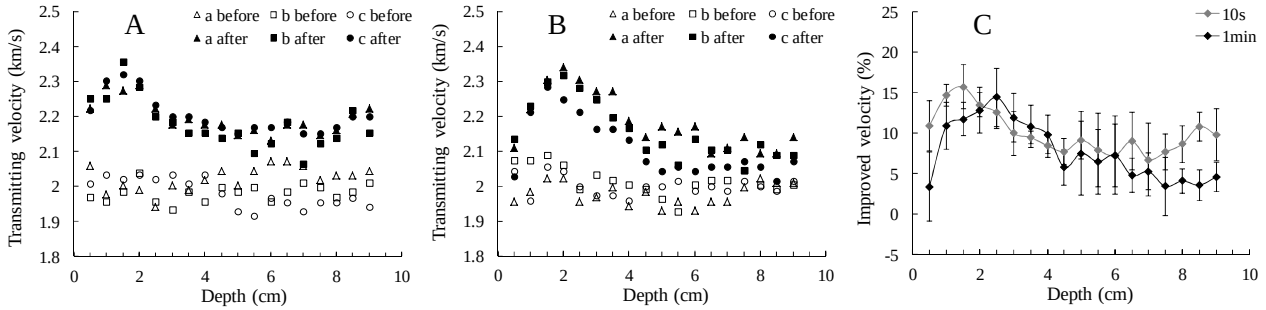

Fig.4 Ultrasound velocity change for the two-step bio-deposition treatment (A: 10 s; B: 1 min; C: increased velocity after treatment)

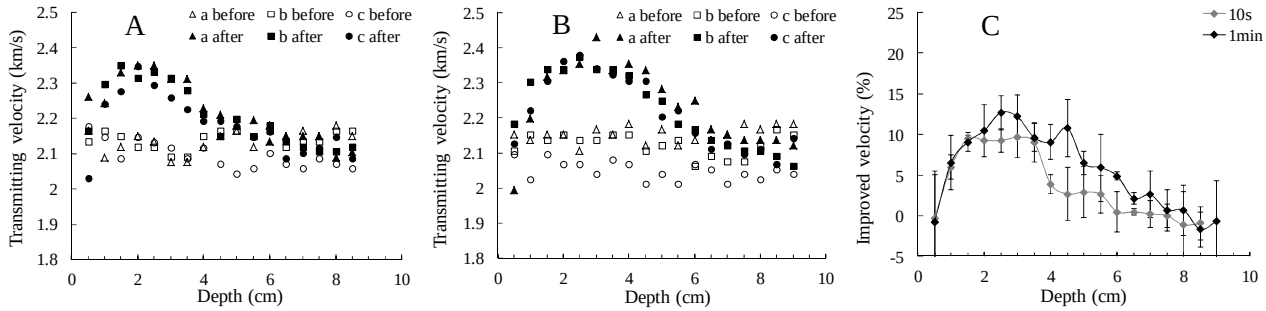

Fig.5 Ultrasound velocity change for the one-step bio-deposition treatment (single treatment, 10s (A) and 10 min (B); C: increased velocity after treatment)

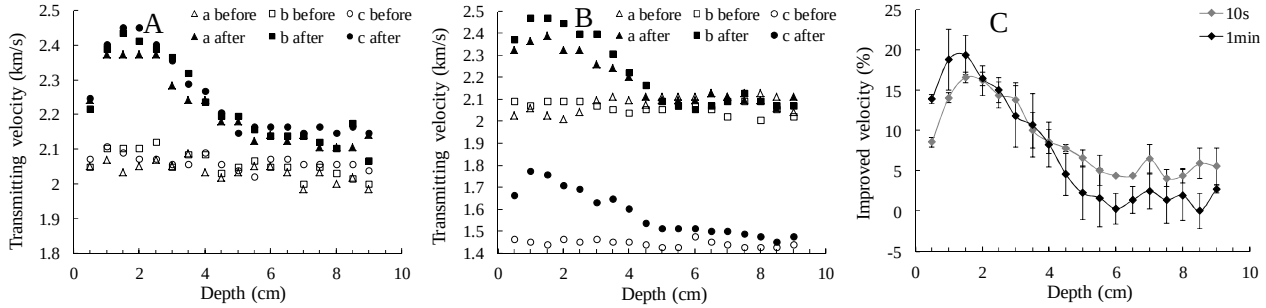

Fig.6 Ultrasound velocity change for the one-step bio-deposition treatment (double treatment, 10 s (A) and 10 min (B); C: increased velocity after treatment)

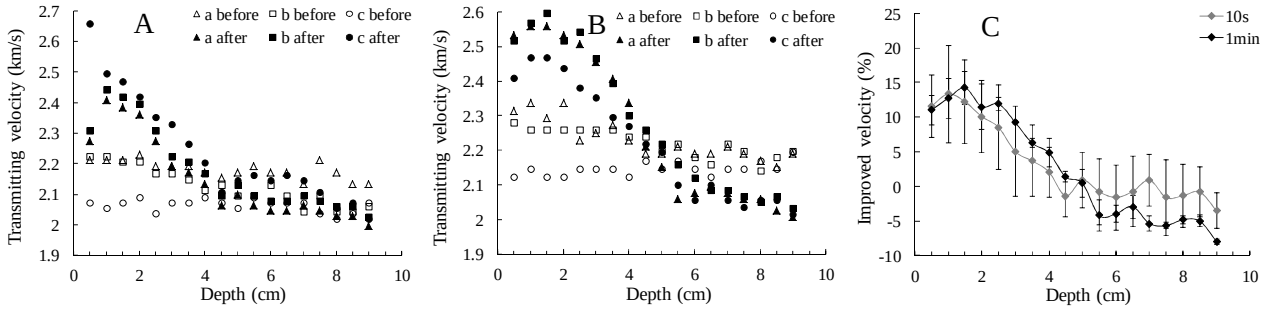

Fig.7 Ultrasound velocity change for the one-step bio-deposition treatment (triple treatment, 10 s (A) and 10 min (B); C: increased velocity after treatment)

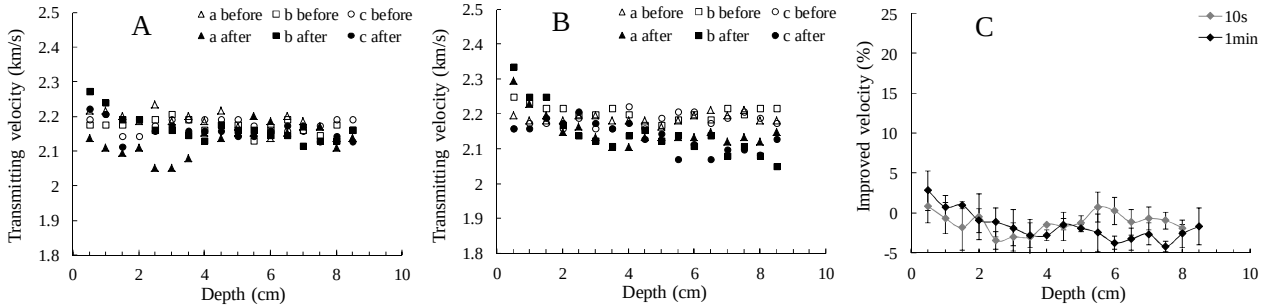

Fig.8 Ultrasound velocity change for the specimens treated by ethyl silicate for 10 s (A) and 1 min (B), and velocity change (C)

Conclusions

In this study, a novel biodeposition treatment was used to strengthen limestone. It was found that the best efficiency was achieved in a double one-step treatment (with combined application of bacteria and nutrients), which brought about 10~20% increase in the transmitting velocity of ultrasonic waves, indicating a great consolidating effect in the matrix. The highest increase was found at around 2 cm below the surface. Chemical treatment by use of ethyl silicate, using the same contact time, did not lead to a significant consolidation.

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